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A titrimetric method of determining sulfates has been modified and adapted to the use of ceric sulfate as the standard oxidant, which depends upon the fact that moist precipitated barium oxalate reacts quantitatively with dissolved sulfates of certain metals to give barium sulfate and the soluble oxalates of these metals. The latter is filtered, washed, made up to volume and an aliquot titrated with standard ceric sulfate solution at 50°C., using ICl as a catalyst and o-phenanthroline ferrous complex as indicator.

The cerometric method has been shown to be capable of giving results which are within ±0.10 per cent of the results obtained by the gravimetric precipitation and by the permanganate method. Results may be duplicated on the same sample with a precision of about ±0.10 per cent.

A study has been made of the effect of the interference of common cations, anions and certain salts. Those anions whose barium salts are more insoluble than barium oxalate in alkaline solution, those ions which are reducing agents to ceric sulfate, those cations whose oxalates are more insoluble than barium oxalate and whose hydroxides are more soluble than their own oxalates and salts which may form soluble complexes with barium oxalate must be absent.

The advantages of the cerometric method over the permanganate method are, greater stability of the standard oxidant, the titration is more easily carried out, the single valence change for cerium eliminates possibility of intermediate or side reactions, and the standard solution is more easily prepared.

The cerometric method is more rapid and less tedious than the gravimetric precipitation method, but since the precipitation must be carried out in alkaline solution is subject to more interference.

A CEROMETRIC METHOD OF DETERMINING SULFATES

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A CEROMETRIC METHOD OF DETERMINING SULFATES

INTRODUCTION

Recent investigations in the application of ceric sulfate as an improved standard oxidant, to be used in place of the less desirable reagents potassium permanganate or dichromate, have resulted in many diversified titrimetric oxidation reactions (7,12,13,14,15,22,27,28, 29,30). At first thought, ceric sulfate might be considered too difficult to purify and, therefore, too expensive to be used extensively in analytical procedures. However, pure salts are not required since the reagent can be conveniently standardized (7,12,13,21,27). A pure salt, hexanitrato ammonium cerate, is now available that may be used as a primary standard (23). However, it is difficult to weigh a salt having an equivalent weight of 548.26 grams with sufficient accuracy to obtain a reliable primary standard.

Quadrivalent cerium is a powerful oxidizing agent in acid solution; the normal oxidation potential being 1.46 volts in normal sulfuric acid or 1.443 volts in two normal sulfuric acid at 25°C., referred to a hydrogen electrode in the same acid (15,21). Ceric sulfate can not be employed in faintly acid, neutral or basic solutions as perceric compounds will be formed.

The chief advantages of ceric sulfate solutions are; stability even on boiling, capability of use in hydrochloric acid medium and simplicity of the reaction, there being only one possible reduction product, namely Ce^{+++}.

$$Ce^{++++} + e \rightleftharpoons Ce^{+++}$$

Among the indicators used for cerometric titrations is the organic compound O-phenanthroline ferrous complex first described by Blau (3) in 1898 and investigated by other workers (22,25,26). In the formation of the complex, three molecules of o-phenanthroline combine with one molecule of ferrous ion. The molar redox potential is 1.14 volts, referred to the hydrogen electrode. At room temperature the ferrous complex is only slowly decomposed by strong acids or by Co^{++}, Cu^{++}, Ni^{++}, Zn^{++}, and Cd^{++}. The blue ferric complex remains almost unchanged by a small excess of a strong oxidizing agent. When a reducing agent is added, the blue complex, at the equivalence point, changes sharply into the reddish ferrous complex. This indicator is stable indefinitely in solution form.

In the present work a method has been adapted to the use of ceric sulfate as the standard oxidant in the determination of sulfates and a study has been made of the conditions necessary for the best results.

PRELIMINARY STUDIES

A complete survey of the titrimetric methods for the determination of sulfates was necessary in order that the most applicable method might be adapted to a cerometric process. In brief the available methods are summarized as follows.

(a). The use of potassium dichromate as the standard precipitant (1,4): The method depends upon the precipitation of the sulfate with an excess of standard barium chloride solution, the excess of the latter then being titrated with potassium dichromate solution using methyl red as an indicator.

(b). The hydrolysis of a salt of a weak acid and a strong base (2,5,8): This method depends upon the precipitation of the sulfate with a standard barium chloride solution with the excess barium being precipitated by an excess of a standard sodium carbonate solution. The precipitate is filtered and the excess carbonate in the filtrate is titrated with standard acid. A modification of this method (19) titrates the excess barium with standard sodium carbonate solution, after precipitation with barium chloride solution.

(c). The use of barium phosphate (10): This method depends upon the precipitation of the sulfate from an acid solution with a slight excess of barium phosphate.

The solution is made basic with sodium hydroxide and the precipitate filtered. The filtrate is heated and ammonium molybdate added, the precipitate dissolved in an excess of standard acid and the excess titrated with standard base.

(d). Internal indicators for direct titration of the sulfate (9,16,24): The first use of an internal indicator for the direct titration with standard barium chloride solution was with rhodizonic acid. The solution is titrated with standard barium chloride solution and the excess titrated with standard sodium carbonate, or a spot plate can be used. The barium chloride precipitates the sulfate and also the barium salt of rhodizonic acid, on back titration the excess barium is removed with sodium carbonate and the indicator changes form and color. In order to make such a direct method more applicable, tetrahydroxyquinone has been developed as an internal indicator (18,20). This method does not require a back titration, the sulfate being titrated with a standard barium chloride solution in a neutral solution and in the presence of isopropyl alcohol to lower the solubility of barium sulfate.

It was obvious that none of the above methods could be adapted to a cerometric method of determining sulfates.

However, Rivett (17) has developed a potassium permanganate method for the determination of sulfate which depends upon the fact that moist precipitated barium oxalate reacts quantitatively by double decomposition with dissolved sulfates of certain metals to give barium sulfate and the soluble oxalates of these metals. The latter is made up to volume, filtered and then titrated with standard potassium permanganate solution. In the present work this method was modified and adapted to the use of ceric sulfate as the standard oxidant.

The reaction of sulfate with barium oxalate is not rapidly completed at ordinary temperatures, but provided the amount of sulfate present is not too great, a few minutes boiling will suffice to complete the reaction. Since the reaction is slow it is apparent that any occlusion will be avoided to a very great extent since only a small amount of the barium oxalate will react with an equivalent amount of sulfate to precipitate barium sulfate. The small error caused by the slight solubility of barium oxalate in water can be avoided by running a blank determination.

Rivett (17) after precipitating the sulfate with barium oxalate made the solution up to volume and used an approximate correction to compensate for the volume

occupied by the precipitate. Since such a procedure is questionable, in the present work the solution was filtered and washed before it was made up to volume. The time of boiling was found to be of much importance and continued stirring by mechanical means was found to aid the complete precipitation of all the sulfate.

Iodine monochloride is used as a catalyst in the reaction between ceric sulfate and oxalate ion. In the early work it was shown that iodine monochloride was a suitable catalyst between arsenite and ceric sulfate (12,21,27,29) at room temperature. Willard and Young (27) found that titration of oxalate in hydrochloric acid containing iodine monochloride proceeded rapidly and quantitatively at 50°C. Iodine monochloride was chosen, although iodide or iodate worked equally well, because it required no blank correction in the volume of ceric sulfate solution used, since the final form of the catalyst in all cases was iodine monochloride. The catalytic action of the iodide or iodate seemed a little slower than that of iodine monochloride, and the blank necessary for the former was an objection.

The action of the catalyst in this reaction is not clear. Iodine monochloride is not reduced at all by oxalate in hydrochloric acid solution in thirty minutes nor does it catalyze at 50°C. the action of oxalate in

hydrochloric acid solution with potassium permanganate, potassium dichromate or potassium iodate. Its catalytic action seems to be confined to the ceric salt titration and this suggests the possibility that the ceric ion is an important factor, since cerous salts were found not to be catalyzed with iodine monochloride and oxalate.

EXPERIMENTAL STUDIES

PREPARATION OF REAGENTS

Ceric Ammonium Sulfate, 0.1 N. This solution was made by dissolving 65-66 grams of ceric ammonium sulfate in 500 ml. of a solution containing 28 ml. of concentrated sulfuric acid and diluting to one liter.

Iodine Monochloride, 0.005 M. This solution was made as follows: 0.279 gram of potassium iodide and 0.178 gram of potassium iodate were dissolved in 250 ml. of water and then 250 ml. of concentrated hydrochloric acid added. The end point was determined by balancing with 0.005 M potassium iodate or 0.005 M potassium iodide in the presence of chloroform, until the pink coloration in the chloroform layer was almost colorless. The reaction is as follows:

$$2KI + KIO_3 + 6HCl \rightarrow 3KCl + 3ICl + 3H_2O$$

o-Phenanthroline Ferrous Complex, 0.025 M. This solution was made by dissolving 6.95 grams of ferrous sulfate heptahydrate in 1000 ml. of water and 14.85 grams of O-phenanthroline monohydrate were added, followed by stirring until the salts were completely dissolved. One drop of this indicator was used for each titration in a volume of 100 - 150 ml.

Barium Oxalate. The barium oxalate was precipitated

by mixing saturated solutions of barium chloride and sodium oxalate, filtering and washing the precipitate free from chloride and oxalate.ions.

STANDARDIZATION OF CERIC SULFATE SOLUTION

Procedure: Weigh 0.1675 gram of sodium oxalate and brush into a 250 ml. beaker. Dissolve by adding 20 ml. of concentrated hydrochloric acid diluted with water to 95 ml. Stir until dissolved, add 5 ml. of 0.005 M iodine monochloride solution and heat to 50°C. Add one drop of O-phenanthroline ferrous complex indicator and using a thermometer as a stirring rod, titrate with standard ceric sulfate solution until the solution is a faint blue color and there is no return of any pink coloration after an interval of one minute. If the temperature falls below 45°C. reheat the solution to 50°C. The weight of oxalate used is equivalent to 25 ml. of N/10 sodium oxalate solution.

The reaction involved is as follows:

$$Na_2C_2O_4 + 2Ce(SO_4)_2 \rightarrow Na_2SO_4 + 2CO_2 + Ce_2(SO_4)_3$$

DETERMINATION OF SULFATE

Procedure: Weigh accurately a sample of between 1 and 2 grams into a beaker and dissolve in about 100 ml. of water. If the solution is acidic to litmus, carefully neutralize with sodium hydroxide (Note 1). Add to the solution a moist paste of barium oxalate in amount to about three times that calculated to precipitate all of the sulfate (Note 2). Heat to boiling and stir from fifteen to thirty minutes at this temperature by means of a mechanical stirrer (Note 3), cool to room temperature and filter on an extracted paper into a 250 ml. volumetric flask. Wash the precipitate with not over 50 ml. of water (Note 4), and dilute the filtrate to the mark shaking thoroughly.

Measure by means of a burette 25 ml. aliquots into a 250 ml. beaker, add 70 ml. of hydrochloric acid (1:4), 5 ml. of iodine monochloride solution and heat to 50°C. (Note 5). Add one drop of o-phenanthroline ferrous complex indicator and using a thermometer as a stirring rod titrate with standard ceric ammonium sulfate solution until the solution is a faint blue color and there is no return to a pink coloration after an interval of one minute. If the temperature of the solution falls below 45°C. reheat the solution to 50°C.

From the volume of ceric ammonium sulfate solution

subtract the volume required by a blank determination which must be made to account for the slight solubility of barium oxalate, and calculate the percentage of sulfur trioxide.

NOTES

Note 1. Sodium hydroxide is used to neutralize any acid that may be encountered due to the hydrolysis of some sulfate salts, since it will not be lost through volatilization. The solution must be neutral or basic because any acid present will tend to dissolve some of the barium oxalate and thus prevent correct results by freeing more oxalate ions than should be.

Note 2. The calculation of the barium oxalate necessary to completely precipitate the sulfate is best assumed on the basis of 100 per cent sulfate present.

Note 3. Boiling of the solution increases the solubility of the barium oxalate and stirring by mechanical means will hasten the reaction between barium oxalate and sulfate, which is slow because of the small solubility of barium oxalate. Complete precipitation will occur within thirty minutes.

Note 4. Since barium oxalate is sparingly soluble in cold water, a minimum amount of water must be used to wash the precipitate to prevent excess of oxalate

from being dissolved. Experience has shown 50 ml. of water to be sufficient.

Note 5. Experiments have shown that oxalate titrations with standard ceric sulfate solution, using iodine monochloride as a catalyst, can be carried out in the presence of hydrochloric acid at a temperature of 50°C. without any special precautions.

The results of the determination of sulfates by the above procedure are shown in Table I, which also includes for comparison figures obtained by the usual gravimetric precipitation method (11,14).

TABLE I

RESULTS OBTAINED BY THE CEROMETRIC METHOD

Sample Number	Gravimetric $\%SO_3$	Cerometric $\%SO_3$	Deviation from grav. %
10	19.66	19.68	+0.02
11	25.44	25.39	-0.05
12	27.01	26.95	-0.06
13	35.51	35.46	-0.05
14	34.36	34.41	+0.05
15	20.07	20.11	+0.04
16	24.68	24.62	-0.06
17	26.48	26.56	+0.08
18	34.24	34.34	+0.10
19	35.65	35.61	-0.04
20	60.59	60.61	+0.02
21	33.74	33.68	-0.06
22	32.46	32.45	-0.01
23	31.21	31.13	-0.08
24	45.26	45.30	+0.04

For further comparison determinations were also made by titration of another aliquot of the oxalate solution with standard potassium permanganate solution, in the usual manner (11,14). Table II shows a comparison of these results with the cerometric method.

Table II

COMPARISON OF THE CEROMETRIC METHOD WITH THE POTASSIUM PERMANGANATE METHOD

Sample Number	Cerometric method $\%SO_3$	Permanganate method $\%SO_3$	Deviation from $KMnO_4$ %
10	19.68	19.60	+0.08
11	25.39	25.30	+0.09
12	26.95	27.05	-0.10
13	35.46	35.40	+0.06
14	34.41	34.43	-0.02
15	20.11	20.02	+0.09
16	24.62	24.60	+0.02
17	26.56	26.50	+0.06
18	34.34	34.28	+0.06
19	35.61	35.56	+0.05
20	60.61	60.56	+0.05
21	33.68	33.64	+0.04
22	32.45	32.43	+0.02
23	31.13	31.08	+0.05
24	45.30	45.25	+0.05

DISCUSSION

The sulfate samples used were the analyzed samples that have been used in Quantitative Analysis courses at Oregon State College for the usual gravimetric precip-

itation method for determining sulfates. Samples from 10 to 19 inclusive were specially prepared sulfate samples supplied from the trade channels and the remainder were pure sulfate compounds such as ammonium sulfate, magnesium sulfate, etc.

The percentage figures are the averages of several determinations. Titration with standard ceric sulfate solution is capable of giving results for sulfates which are within ±0.10 per cent of the value obtained by the gravimetric and permanganate method. Results may be duplicated on the same sample with a precision of about ±0.10 per cent.

INTERFERENCE STUDIES

A study was made of the effect on the method by the presence of most of the common cations and anions and of certain salts. The results are shown in Table III.

The interfering ions may be divided into the following classes: (a) those anions whose barium salts are more insoluble than barium oxalate in alkaline solution, such as phosphate, arsenate, chromate, borate, and carbonate; (b) those ions which are reducing agents towards ceric sulfate, such as iodide, ferrocyanide, arsenite, thiosulfate, nitrite, sulfide, thiocyanate, mercurous, stannous, ferrous, and antimonous; (c) those cations

TABLE III

INTERFERENCE STUDIES

Salt used	Diverse sub. present	gm.	%SO_3 found	present	Deviation %
K Alum.	Al^{+++}	0.162	33.68	33.68	0.00
$CdSO_4:3\frac{1}{2}H_2O$	Cd^{++}	0.621	31.13	31.13	0.00
$Fe(NO_3)_3 \cdot 9H_2O$	Fe^{+++}	0.271	49.91	45.30	+4.61
K_2SO_4	K^+	0.675	45.30	45.30	0.00
$MgSO_4 \cdot 7H_2O$	Mg^+	0.147	32.45	32.45	0.00
$(NH_4)_2SO_4$	NH_4^+	0.215	60.61	60.61	0.00
NaCl*	Na^+	0.786	45.30	45.30	0.00
$ZnSO_4 \cdot 6H_2O$	Zn^+	0.364	29.47	29.70	-0.23
NaCl*	Cl^-	0.606	45.30	45.30	0.00
$NaC_2H_3O_2$*	$C_2H_3O_2^-$	7.196	47.05	45.30	+1.75
NH_4Cl*	NH_4Cl	5.000	46.35	45.30	+1.05
NH_4NO_3*	NH_4NO_3	2.000	46.26	45.30	+0.96
$NaNO_3$*	$NaNO_3$	2.000	44.92	45.30	-0.38
Na NO_3*	$NaNO_3$	5.000	47.01	45.30	+1.71
Na NO_3*	$NaNO_3$	15.00	51.25	45.30	+5.95
Na NO_3*	$NaNO_3$	25.00	51.29	45.30	+5.99
KNO_3*	KNO_3	5.00	47.06	45.30	+1.76
KNO_3*	KNO_3	15.00	51.30	45.30	+6.00

* The sulfate sample used was potassium sulfate

whose oxalates are more insoluble than barium oxalate and whose hydroxides are more soluble than their own oxalates, such as calcium, strontium, lead, barium, silver, mercuric, manganous, cupric, bismuth, nickelous, and cobaltous.

Rivett (17) has shown that potassium nitrate, ammonium nitrate and sodium acetate interfere in his permanganate method for determining sulfates. He offered the explanation that these salts cause double decomposition with barium oxalate leading to a positive error. In the present work the effects of ammonium chloride and sodium nitrate were also studied and similar results were obtained. It is probably true that such salts react to form soluble complexes. Fales and Thompson (6) as a result of a recent study of the gravimetric precipitation of sulfate have stated that there is evidence which indicates the possible existence of a complex ion or complex-compound form of sulfate in potassium nitrate solutions which retards precipitation under certain conditions. Further they have shown that barium sulfate precipitates formed in the presence of nitrates are more sensitive to influence by variations in conditions of precipitation and treatment than are precipitates formed in the absence of nitrates. It is apparent that nitrates influence the precipitation of barium sulfate.

The advantages of the cerometric method over the permanganate method are: (a) the titration is more easily carried out without any special precautions as to the speed of addition of the standard oxidant or constant stirring; (b) there is no trouble in reading the meniscus of the ceric sulfate solution as is the case with potassium permanganate solution; (c) the single valence change for cerium eliminates possibility of intermediate or side reactions; (d) the standard solution is much more easily prepared than potassium permanganate solution; (e) ceric sulfate solutions do not require frequent standardization. The stability of ceric sulfate solutions has been pointed out by Furman (7) and by Willard and Young (28). Standardizations carried out over relatively long periods of time confirmed their observations that the solution was stable for forty weeks.

The disadvantages of the method are: (a) a catalyst is necessary to complete the reaction between ceric sulfate and oxalate at a low temperature; and (b) the cost of ceric sulfate is higher than that of potassium permanganate.

The cerometric method is more rapid and less tedious than the gravimetric method, but since the precipitation must be carried out in alkaline solution it is subject to more interference.

SUMMARY

A method has been modified and adapted to the use of ceric sulfate as the standard oxidant for the determination of sulfates and the effect of interfering ions and substances has been studied.

The cerometric method is capable of giving results which are within ±0.10 per cent of the results obtained by the gravimetric precipitation method and by the potassium permanganate method, and the results may be duplicated on the same sample with a precision of about ±0.10 per cent, in the absence of interference.

The advantages of the cerometric method over the permanganate method are: (a) greater stability of the standard oxidant; (b) the titration is more easily carried out; (c) the meniscus of the ceric sulfate solution is more easily read; (d) the single valence change for cerium eliminates possibility of intermediate or side reactions; and (e) the standard solution is more easily prepared.

The cerometric method is more rapid and less tedious than the gravimetric precipitation method, but since the precipitation must be carried out in alkaline solution is subject to more interference.

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